

FOREWORD

This report was prepared by the Explosives Research Center of the U. S. Bureau of Mines, under USAF Delivery Order (33-616) 60-8, Project No. 6075, "Flight Vehicle Hazard Protection," Task No. 607504, "Fire and Explosion Characteristics of Aerospace Vehicle Combustibles". It was administered under the direction of the Research and Technology Division, Wright-Patterson Air Force Base, with Mr. Benito Botteri as project engineer. The report covers work done during the period April 1963 to March 1964 and is the fourth annual report on this contract.

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ABSTRACT

This is the fourth in a series of reports on the fire and explosion hazards associated with combustibles and other gases likely to be found in aircraft and missile systems. It presents experimental results pertinent to inhibition of gaseous detonation, ignition of solid oxygen-liquid hydrogen mixtures, and flammability characteristics of halogenated hydrocarbons.

The halogenated hydrocarbons do not appear to be particularly effective inhibitors of gaseous hydrogen-oxygen detonation. Combustibles such as methane and hydrogen were found to be superior to the halogenated hydrocarbons on a weight basis.

Cryogenic mixtures of solid oxygen and liquid hydrogen can be ignited by 0.5-ounce projectiles moving at speeds as low as 1310 ft/sec (400 meters/sec). Ignition appears to occur at shock strengths of 1.5 to 3.0 kilobars.

Although the halogenated hydrocarbons considered here do not appear to be flammable in air at atmospheric pressure and ordinary temperatures, some are flammable in oxygen under these conditions. Flame speeds and maximum explosion pressures associated with the flammable mixtures were found to be considerably lower than those of the corresponding hydrocarbon-oxygen mixtures.

This report has been reviewed and is approved.



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INTRODUCTION

This is the fourth annual report on the fire and explosion hazards associated with combustibles used in aircraft and missile systems. It gives a summary of the results obtained to date from experiments conducted on (1) the suppression of gas phase hydrogen-oxygen detonations, (2) the explosivity of liquid hydrogen-solid oxygen mixtures, and (3) the flammability of halogenated hydrocarbons at elevated temperatures. The first three reports (ref. 1, 2 and 3) presented a general discussion of fire and explosion phenomena and included vapor pressure and flammability characteristics data for a number of combustibles and oxidants.

Although it has been known for some time that mixtures of oxygen crystals and liquid hydrogen are shock sensitive, no quantitative information was available concerning the shock strength required to initiate an explosive reaction. This report presents the results of experiments designed to determine the shock sensitivity of such mixtures. Further, results are presented on the flammability of various halogenated hydrocarbons and on their effectiveness as inhibitors of the initiation of detonation in gaseous hydrogen-oxygen mixtures.

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RESULTS AND DISCUSSION

Suppression of Hydrogen-Oxygen Gas Phase Detonation

An effective detonation inhibitor is defined as one which increases the ignition energy requirements for detonation in a particular system. Consequently, it is only necessary to determine the ignition energy requirements for inhibited hydrogen-oxygen mixtures in order to quantitatively evaluate the effectiveness of a particular inhibitor. Experiments were conducted in an 11.8-inch (30 cm) diameter steel sphere equipped with a means of admitting the desired gas mixtures and recording the explosion pressure at the wall. An exploding wire was used as the ignition source and a piezoelectric transducer was used to record the pressure history; the energy for the ignition wire was obtained from a charged condenser. In these experiments, the minimum stored energy required for initiation of detonation was determined to about ± 5 percent for the majority of the runs. Figure 1 shows the results of this study for a stoichiometric hydrogen-oxygen mixture containing various percentages of the inhibitors methane, methyl chloride, Freon 13B1 (bromotrifluoromethane), Freon 114B2 (1,2-dibromotetrafluoroethane), nitrogen, oxygen and hydrogen. A similar curve labeled "vacuum" shows the effect of reduced pressures on the ignition energy requirements; the abscissa in this case is the percent reduction in pressure. The figure shows that methane and methyl chloride are the best inhibitors of the materials tested to date. Further, reducing the pressure by 20 percent appears to have an insignificant influence on the ignition energy requirements. These results are in agreement with those obtained in an earlier investigation (ref. 4).

Figure 2 presents the data given in figure 1 with the inhibitor concentration expressed as weight percent rather than volume percent. On this basis, hydrogen and methane are not only the best inhibitors of the group but they apparently are equally effective.

Explosivity of Liquid Hydrogen-Solid Oxygen Mixtures

One of the objects of this investigation is the determination of the ignition sensitivity to shocks, of mixtures of solid oxygen and liquid hydrogen. In these experiments the shock sensitivity was determined by bullet impact techniques. A 0.5-inch diameter, 0.5-inch long cylindrical brass slug (0.5 ounce) was fired from a smoothbore rifle into the cryogenic mixture. The projectile velocity was controlled by varying the quantity and type of propellant in the rifle cartridge. The projectile velocity was determined by measuring the time of travel between two fixed points. Photographs of the experimental installation are shown in figures 3 and 4. The rifle shown in figure 4 is mounted to fire down into the shielded enclosure containing the cryogenic mixture. In practice, the rifle was fired remotely from a control building shown in figure 3. Most of the containers for the cryogenic mixture were constructed of 1/32-inch thick cylindrical polyethylene containers embedded in blocks of polyurethane. Liquid regression rate studies showed these containers to be superior to most silvered evacuated glass dewars.

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To conduct an experiment, liquid hydrogen was first poured into the insulated polyethylene container which was then covered and carried into the shielded enclosure. Oxygen gas, metered into the covered container, condensed on contact with the liquid and gaseous hydrogen; samples of boil-off gas indicated that at least 99.5 percent of the admitted oxygen was condensed. The cover was removed remotely and the rifle was fired. Blast gages consisting of two thin metal strips (figure 3) were used to indicate the occurrence of detonation. Experiments were conducted with samples containing 0.63 and 1.27 ounces of solid oxygen in an excess of liquid hydrogen. A muzzle velocity of 1970 ft/sec (600 meters/second) always yielded a positive result; these were evidenced by a loud, sharp acoustic report and by complete (permanent) deflection of the thin strip gage and partial deflection of the thicker strip gage. These results indicated that the explosive yields of liquid hydrogen-solid oxygen mixtures are greater than those for equal weights of TNT.

Experiments conducted in foamed polystyrene containers with muzzle velocities of 1640 ft/sec (500 meters/second) yielded either negative or partial results. When negative results were obtained, there was no apparent sound other than that of the gun report; the strip gages were not deflected, the container was not damaged except by the projectile itself, and oxygen crystals remained in the container after the shot. In a partial result, the acoustic report was appreciably reduced by comparison to that obtained with a positive result, and the thin strip gage was only partially deflected. Experiments conducted with the polyethylene containers gave some positive results at 1640 ft/sec and some partial results at 1310 ft/sec (400 meters/second). It is not yet clear whether this difference was due to the polyethylene or to varying amounts or compositions of the tested mixtures.

Acoustic velocity in liquid hydrogen is about 3940 ft/sec (1.2×10^3 meters/sec) (ref. 5) and the specific gravity of liquid hydrogen is about 0.07. For solid oxygen, the specific gravity of the crystal in the α state is given as 1.426 (refs. 6 and 7). Literature search has not yet yielded a sonic velocity for this crystal phase. The data of Steward (ref. 8) give a sonic velocity of about 4590 ft/sec (1.4×10^3 meters/second) for the γ phase; the α phase is not likely to be appreciably different. The mean volumetric specific gravity of the hydrogen-oxygen mixture is about 0.2 for that portion containing the oxygen crystals. Because of the loose packing of the needle-shaped oxygen crystals and because of the uncertainty in the applicable sonic velocity, the sonic velocity of hydrogen will be assumed applicable to that portion containing the oxygen crystals.

In the tests reported here the projectiles were made of brass with a specific gravity of about 8.8. A projectile velocity of 1970 ft/sec (600 meters/second) is about Mach 0.5 relative to the liquid hydrogen, so that the Bernoulli equation should apply to a description of the deceleration of the projectile. A penetration depth of about 1.4-inch (3.6 cm) would reduce the projectile velocity by about 1 percent and a penetration depth of 13 inches (34 cm) would reduce the projectile velocity by about 10 percent.

Reasonable depths of liquid hydrogen above the oxygen crystals should therefore have little effect upon the test results.

Equating the particle velocity to the projectile velocity and the shock velocity to the sonic velocity, the shock pressure was found to be about 0.5 kilobar (1 Kbar \approx 1000 atmospheres) in the hydrogen and about 1.5 kilobars in the hydrogen-oxygen mixture. Similar acoustic shock approximation calculations give about 10 kilobar for polyethylene and between 0.6 and 1.8 kilobars for foamed styrene depending upon the assumed sonic velocity.

The fact that mixtures in both types of containers gave initiation with nearly similar projectile velocities implies that initiation is not a consequence of compression of a thin film between the projectile and the bottom of the container. The shock strength producing initiation is within the range of 1.5 to 3.0 kilobars; this is a consequence of the possible doubling of the shock pressure upon reflection (in the acoustic approximation). The observations of initiation at 1310 and 1640 ft/sec with polyethylene and 1970 ft/sec with foamed styrene are consistent with the anticipated reflection characteristics.

Flammability of Halogenated Hydrocarbons at Elevated Temperatures

Recent interest in the halogenated hydrocarbons as fire extinguishing agents has led to a thorough investigation of the flammability characteristics of these materials in various atmospheres that might be encountered in missile systems. This report is concerned with five halogenated hydrocarbons in atmospheres of air, oxygen and nitrogen tetroxide. The first experiments were conducted to determine the stability of these materials in the three atmospheres over the temperature range of interest (75° to 1200° F). First, autoignition temperature (AIT) experiments were conducted in the standard Bureau of Mines apparatus (ref. 9) to determine if these halogenated hydrocarbons ignite spontaneously in any of the above atmospheres within this temperature range. The experiments were conducted by adjusting the temperature of the test vessel to the desired value, introducing the oxidizing atmosphere and, after allowing sufficient time for temperature stabilization, injecting the halogenated hydrocarbon (liquid or gas) into the atmosphere with a hypodermic syringe. Table 1 shows the results of these experiments for the five halogenated hydrocarbons in three oxidizing atmospheres. The autoignition temperatures listed in the table indicate the maximum temperatures at which limits of flammability of the various compounds can be measured reliably in their respective atmospheres; for example, since Freon 114B2, or more simply 114B2, ignites spontaneously in an oxygen atmosphere in a glass vessel at temperatures above 860° F, limits of flammability should only be determined for this fuel-oxidant combination at temperatures below 860° F.

TABLE 1. - Autoignition temperatures (°F) of various halogenated hydrocarbons in air, oxygen and nitrogen tetroxide atmospheres in glass containers.

Halogenated Hydrocarbon	Code	Oxidant		
		Air	Oxygen	Nitrogen Tetroxide
CF ₂ BrCl	12B1	>1200*	1090	>1200*
CF ₂ Br ₂	12B2	>1200*	1100	>1200*
CF ₃ Br	13B1	>1200*	>1200*	1090
CBrF ₂ ·CBrF ₂	114B2	1050	860	910
CH ₂ BrCl	--	840	690	630

* This is meant to imply that if autoignition occurs, the AIT value is greater than 1200° F.

It was observed that following autoignition of both 12B2 and 114B2 in air or oxygen, the glass test vessel was etched; further, an analysis of the product gases showed they contained appreciable quantities of SiF₄ in the latter case. Since the glass vessel may have affected the AIT results, similar experiments were conducted with 114B2 in air in a stainless steel vessel. In this case, 114B2 did not autoignite in air at temperatures to 1200° F; however, when a short length of glass rod was introduced into the stainless steel vessel at 1200° F, ignition occurred immediately. After the glass rod was removed from the vessel, autoignition was obtained at temperatures as low as 1076° F. Apparently trace quantities of silicon-containing compounds affect the AIT of 114B2 appreciably. It was observed while conducting the AIT experiments that although the various halogenated hydrocarbons did not ignite below the temperatures indicated in table 1, there was evidence that a chemical reaction had occurred at lower temperatures. The presence of such a reaction could appreciably affect the results of any limit-of-flammability experiments that might be conducted, particularly if the half-life of the reaction were comparable to the time required to prepare and test the desired gas mixture. In view of this, a simple kinetic experiment was devised and conducted to obtain a quantitative measure of the rate of oxidation of 12B2 (one of the more stable of the halogenated hydrocarbons studied here) in oxygen at atmospheric pressure over the temperature range from 75° to 1200° F in a glass reaction vessel. A quantitative measure of the reaction rate at each temperature was obtained by measuring the loss of 12B2 and the carbon dioxide generated during a one minute period; the product gases were analyzed with a gas chromatograph. Table 2 gives the results of these experiments. These indicate that the reaction has a half-life of one minute at some temperature between 800° and 950° F. Spot tests on the remaining halogenated hydrocarbons indicated that none of them showed any evidence of reaction at temperatures below 500° F. Accordingly, it was decided to conduct preliminary experiments that would quickly determine approximate limits of flammability for these halogenated hydrocarbons in the

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various oxidizing atmospheres at temperatures below 500° F. The apparatus used in these studies consisted of a 2-liter glass sphere and an 8.5-liter stainless steel sphere equipped with a piezoelectric pressure transducer for use in determining the pressure rise during combustion. The entire apparatus was placed in a large oven whose temperature could be maintained uniform to 500° F. The results of these experiments are shown in table 3 for each of the halogenated hydrocarbons in atmospheres of air and oxygen at the temperatures indicated. These results show that CH₂BrCl and 12B2 have flammable zones when mixed with oxygen in both glass and steel vessels. However, it was observed in the glass vessel experiments with 12B2 that flames would propagate upward away from the ignition source but never downward.

TABLE 2. - Yield of carbon dioxide in an oxygen atmosphere at various temperatures for a reaction period of one minute in a glass vessel.

Temperature °F	Concentration after one minute, vol. %	
	12B2*	CO ₂
75	17	0
500	17	0
800	10	2
950	1	9
1100	0	11

* Initial concentration = 17 volume percent.

TABLE 3. - Limits of flammability of various halogenated hydrocarbons (volume percent) in glass and stainless steel.

Halogenated Hydrocarbon	Code	Glass Container				Stainless Steel Container				Tempera- ture, °F
		Air		Oxygen		Air		Oxygen		
		LL	UL	LL	UL	LL	UL	LL	UL	
CF ₂ BrCl	12B1	NF		NF		NF		NF		75
CF ₃ Br	13B1	NF		NF		NF		NF		75
CF ₂ Br ₂	12B2	NF		28-30	80-85	NF		31-33	70-75	122
CH ₂ BrCl	--	NF		*EXPL		NF		9-10	>85	212
CBrF ₂ ·CBrF	114B2	NF		--	--	NF		20-21	52-53	212

LL: Lower limit *EXPL - Apparatus was demolished by an explosion on
 UL: Upper limit the first near-lower limit test.
 NF: Nonflammable

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An apparatus was constructed to determine the combustion pressure histories for those halogenated hydrocarbon-oxygen mixtures previously shown to be flammable (figure 5). The two-foot diameter spherical test vessel shown in the figure is equipped with a piezoelectric pressure transducer and a central ignition source. Specific gas mixtures can be prepared in the apparatus with the composition known to at least ± 0.1 volume percent; use is made of a hot-wire gas detector bridge which works on a null balance principle. An accurately prepared sample of the halogenated hydrocarbon-oxygen mixture to be tested is added to both gas cells, and the bridge is balanced with a precision differential voltmeter. The gas pump is started and halogenated hydrocarbon is added gradually to the system; gaseous halogenated hydrocarbons are added to the system through the piping indicated in figure 5 and those that are normally liquids are added as liquids and vaporized in the gas stream on a 36-inch asbestos wick. A small portion of the pumped gas is purged through the sample gas cell. Addition of halogenated hydrocarbon is continued until the bridge again attains a null state, indicating that the halogenated hydrocarbon concentration of the gas mixture in the sphere and related piping is the same as that in the standard gas cell.

Since an appreciable quantity of bromine gas is generated when brominated hydrocarbons are burned, a 12-foot long, 4-inch diameter sodium thiosulfate adsorption column was incorporated into the vent system to remove the bromine prior to dumping the products into the outside atmosphere. To conduct an experiment, the desired gas mixture is first prepared in the apparatus then the mixture is ignited by fusion of a short length of No. 40 nickel wire wrapped with 50 mg of guncotton. The pressure history following ignition is recorded by means of a piezoelectric pressure transducer in conjunction with an electronic amplifier and an oscilloscope. A series of three duplicate experiments was conducted on each of the three halogenated hydrocarbons investigated. For each of the three mixtures examined, the concentration of halogenated hydrocarbon was chosen near the middle of the flammable zone as shown in table 3. A typical pressure record obtained from these experiments is shown in figure 6. Table 4 summarizes the results of these experiments for each of the gas mixtures investigated. Comparison of these results with those obtained with methane shows that flame speeds through the halogenated hydrocarbon-oxygen mixtures are apparently about 1000 times slower than corresponding flame speeds through the methane-oxygen mixtures. Rates of pressure rise are correspondingly very low in comparison to those from hydrocarbon-oxygen.

The maximum explosion pressures developed by the combustion of 12B2-oxygen mixtures (table 4) are very low compared with those developed by the combustion of near-stoichiometric methane-oxygen mixtures. Further, although the pressures developed in the combustion of 114B2 and CH_2BrCl -oxygen mixtures are about a factor of 10 larger than those developed with 12B2-oxygen mixtures, they are still low compared with those obtained with stoichiometric hydrocarbon-oxygen mixtures.

The bromine concentrations found in the combustion products of some of the mixtures investigated here are listed in table 4. The presence of such large quantities of bromine in the product gases poses a toxicity problem where these halogenated hydrocarbons are used in oxygen-rich atmospheres.

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TABLE 4. - Maximum pressures, rates of pressure rise and bromine concentrations developed during combustion of three halogenated hydrocarbons in an oxygen atmosphere.

Halogenated Hydrocarbon	Code	Mixture composition (vol. %)		P _{max} (psig)	τ (sec)	P _{max} / τ (psi/sec)	Bromine concentration (vol.%)
		Combustible*	Oxygen				
CF ₂ Br ₂	12B2	50	50	6.1	2.3	2.6	--
		51	49	5.3	2.1	2.5	--
		50	50	3.8	1.5	2.5	--
		49	51	--	1.6	--	13
CBrF ₂ ·CBrF ₂	114B2	31	69	54	ca. 4	--	15
		31	69	31	5	6.2	20
		28	72	67	4	17	21
		30	70	71	3.5	20	21
CH ₂ BrCl	--	16	84	75	1	75	--
		16	84	79	1	79	--

* Halogenated hydrocarbon.

SUMMARY AND CONCLUSIONS

The halogenated hydrocarbons, 114B2 and 13B1, appear to be better suppressants of detonation in gaseous hydrogen-oxygen mixtures on a volume percent basis than supposedly inert diluents such as nitrogen; however, methane and methyl chloride are still better than either 114B2 or 13B1.

The shock strength that produces initiation of solid oxygen-liquid hydrogen mixtures appears to be in the vicinity of 1.5 to 3.0 kilobars. Initiation has been obtained by impact of a 0.5 ounce projectile moving at speeds as low as 1310 ft/sec.

The halogenated hydrocarbons investigated in this study appear to react with oxygen-containing atmospheres at temperatures above 500° F. With the exception of Freon 13B1, these materials also autoignite in oxygen atmospheres below 1200° F; Freon 114B2 and CH₂BrCl autoignite in atmospheres of air, oxygen, and nitrogen tetroxide at temperatures below 1200° F. Flammable zones were not found at 75° F with Freon 12B1 and 13B1 in either air or oxygen atmospheres; however, Freon 12B2 and CH₂BrCl form flammable mixtures in oxygen at 122° and 212° F, respectively. The flame speeds and maximum explosion pressures associated with combustion of confined halogenated hydrocarbon-oxygen mixtures are smaller than those associated with the combustion of confined hydrocarbon-oxygen mixtures. However, considerable quantities of bromine gas are produced during the combustion of the brominated materials in oxygen.

PROPOSED INVESTIGATIONS

The study of the shock sensitivity of the liquid hydrogen-solid oxygen system initiated here should be continued. Further, additional halogenated hydrocarbons should be evaluated to determine their effectiveness as inhibitors of the gaseous hydrogen-oxygen detonation and their combustion properties in various oxidizing atmospheres.

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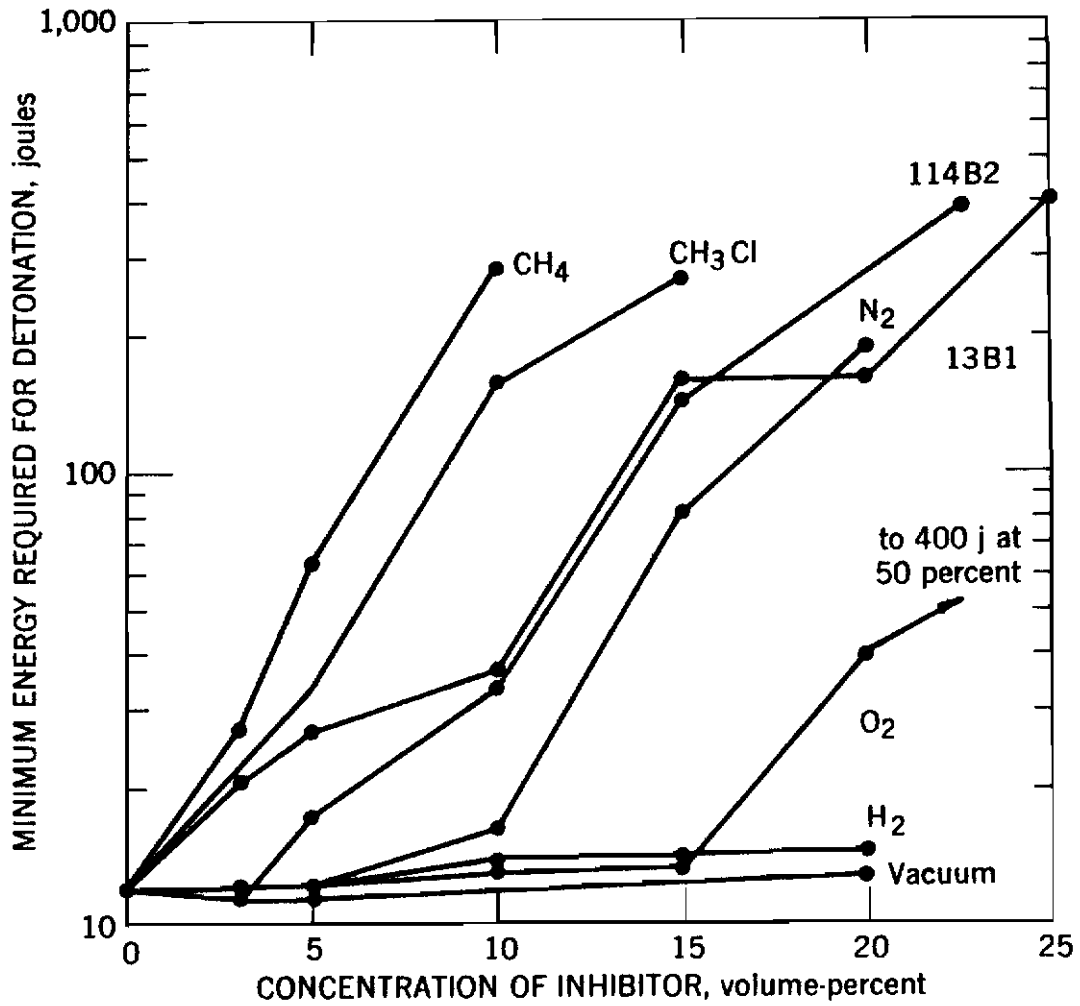


Figure 1. - Minimum stored ignition energies required for initiation of detonation of stoichiometric hydrogen-oxygen mixtures as a function of inhibitor concentration (volume percent).

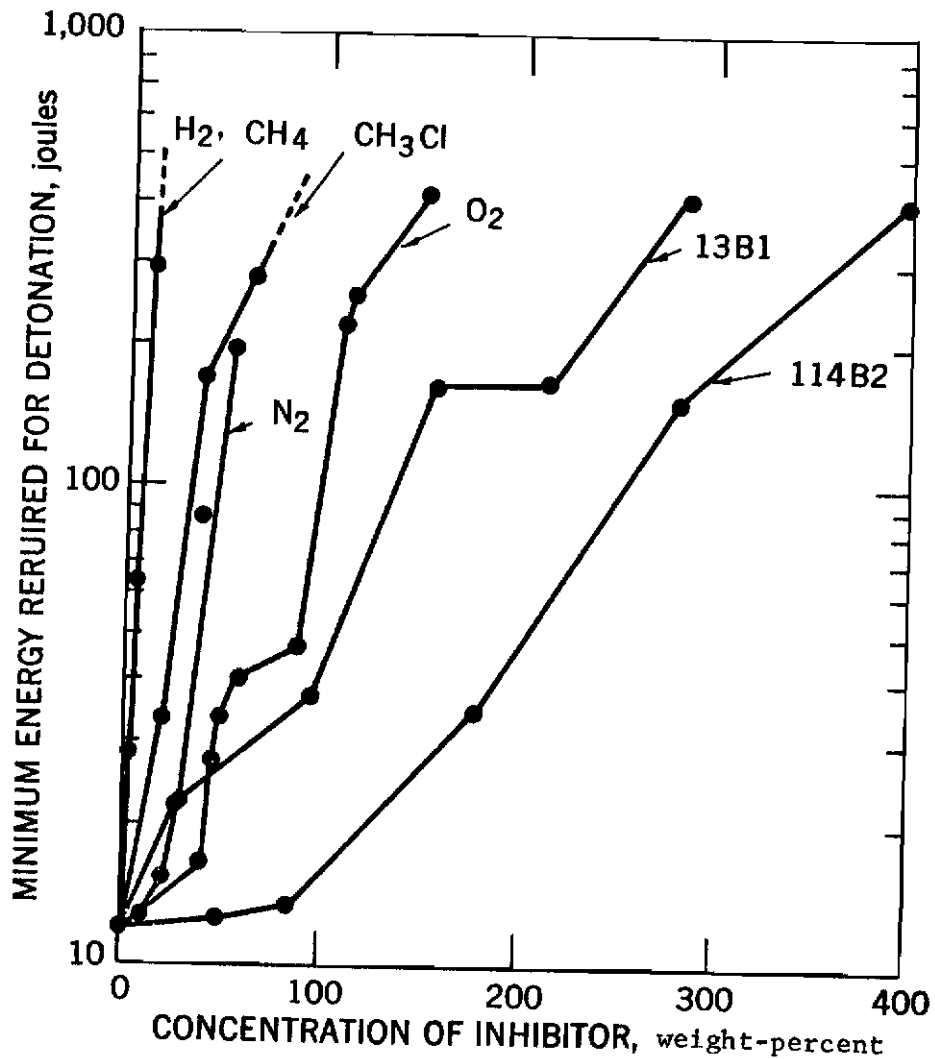


Figure 2. - Minimum stored ignition energies required for initiation of detonation of stoichiometric hydrogen-oxygen mixtures as a function of inhibitor concentration (weight percent).



Figure 3. - Facility used to conduct experiments on shock sensitivity of solid oxygen-liquid hydrogen mixtures.

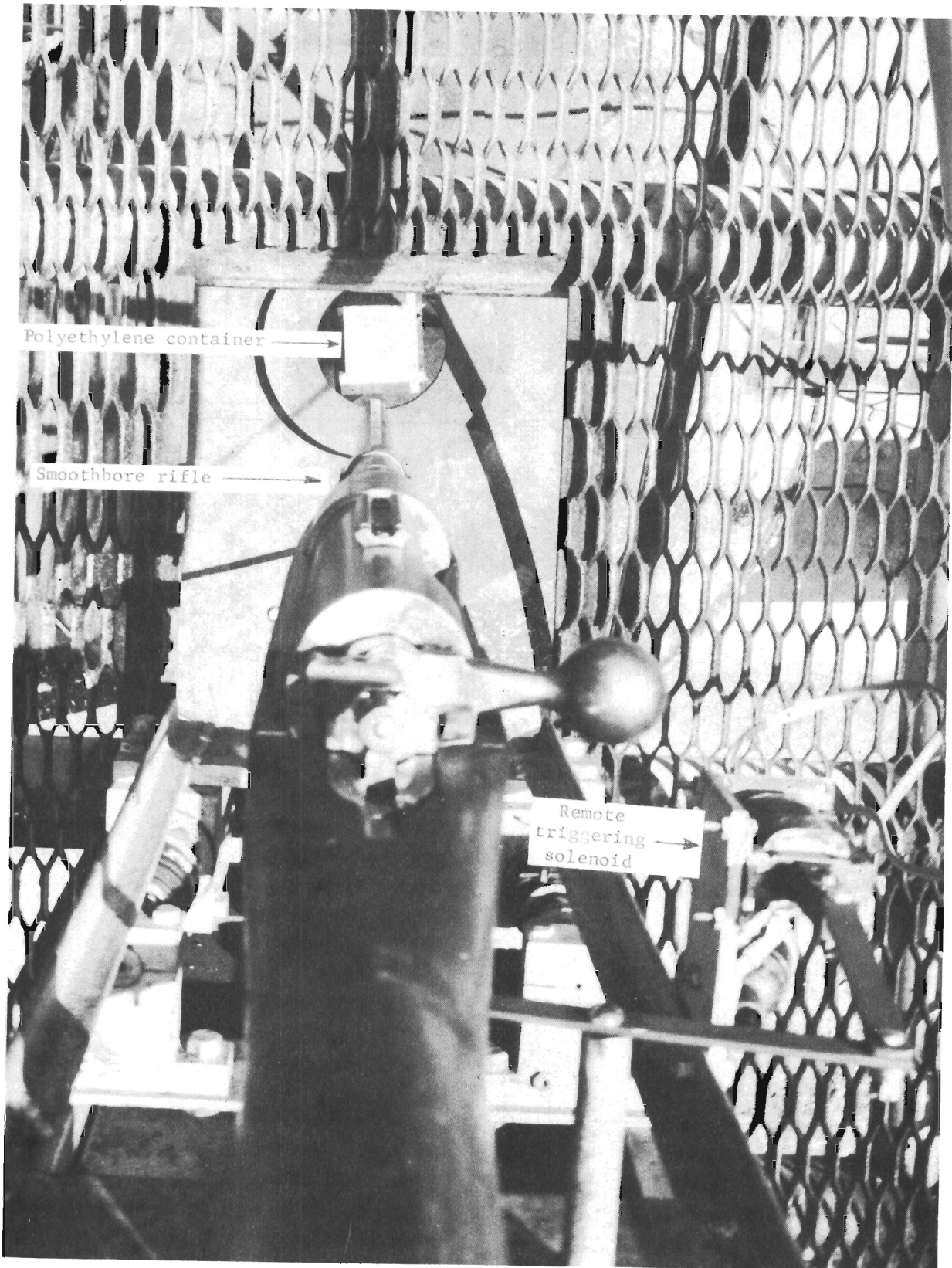


Figure 4. - View inside explosion enclosure showing polyethylene container and blast gages used for shock sensitivity experiments.

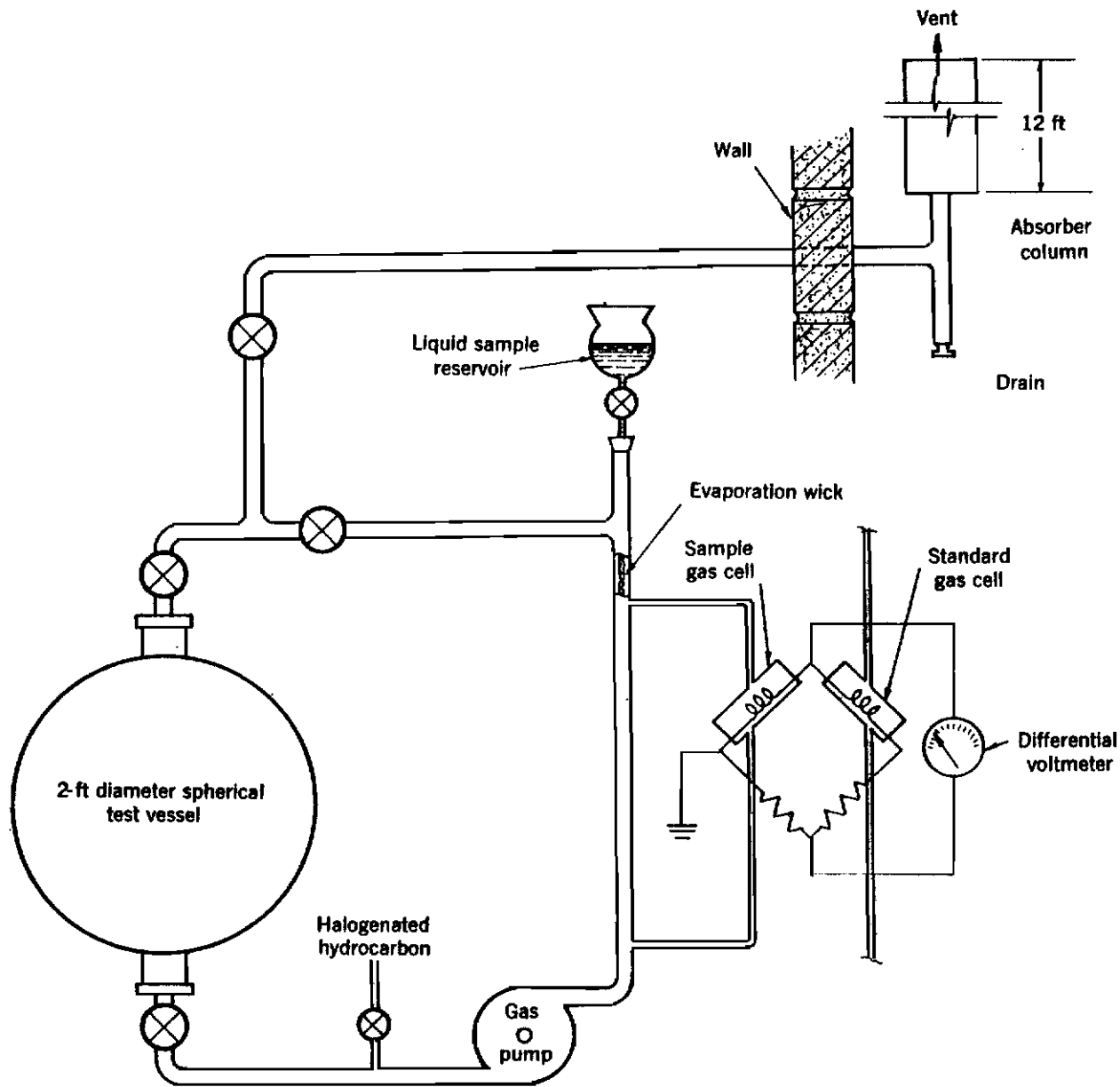


Figure 5. - Apparatus used to measure rates of pressure rise and maximum explosion pressures of various confined flammable gas mixtures.

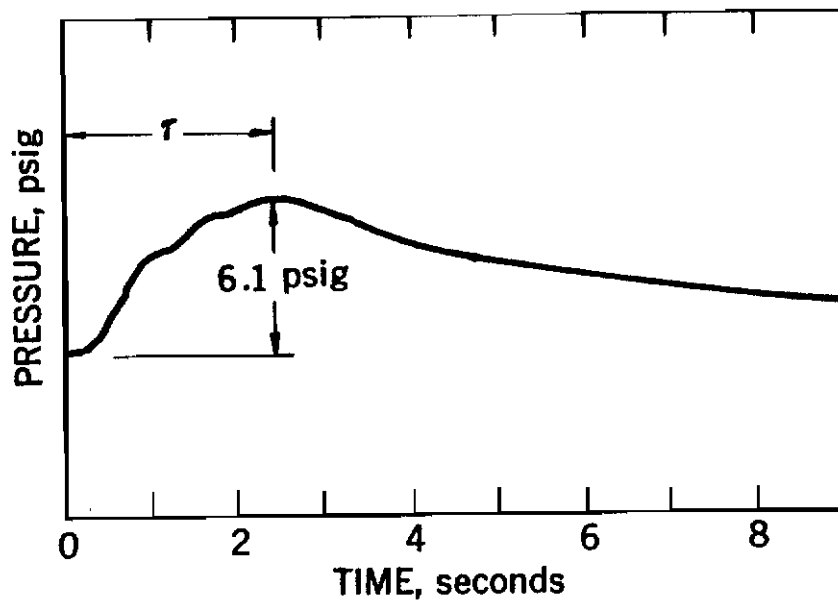


Figure 6. - Typical pressure history record obtained during combustion of 50 volume percent CF_2Br_2 in an oxygen atmosphere in a 2-foot diameter sphere.